

APPENDIX 4 for  
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# SOL-GEL SCIENCE

The Physics and Chemistry of  
Sol-Gel Processing

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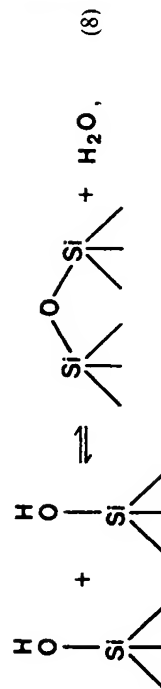
imposed by the adsorbate or limited accessibility to the surface, values less than  $4.9 \text{ OH/nm}^2$  are observed. For example, Peri and Hensley [41] found the surface coverage of methoxide groups (OMe) to be  $4\text{--}5 \text{ OMe/nm}^2$ . Stöber *et al.* [45] autoclaved silica with anhydrous alcohol for six hours at  $200^\circ\text{C}$ . For normal alcohols, OR surface coverage decreased with the alkyl chain length:  $4.7 \text{ OMe/nm}^2$ ,  $3.7 \text{ OEt/nm}^2$ ,  $3.5 \text{ OPr/nm}^2$ , and  $3.2 \text{ OBu/nm}^2$ . Of course for branched alcohols the surface coverage is strongly dependent on steric factors. Iler [1] states that for branched alcohols it has been established experimentally that each alcohol molecule will cover  $0.14n \text{ nm}^2$  where  $n$  is the "branch" number defined as the width of the hydrocarbon groups at their widest point if "spread out flat." This expression holds for  $n > 2$ ; however it is doubtful that this relation pertains to irregular surfaces characterized by  $2 \leq d_s \leq 3$ .

### 3.

#### DEHYDROXYLATION

The high surface areas of gels, combined with surface hydroxyl coverages of  $4.9 \text{ OH/nm}^2$  and additional physically adsorbed water, result in quite large quantities of water ( $\text{OH} + \text{H}_2\text{O}$ ) bound to air-equilibrated porous gels. For example a silica gel with a BET surface area of  $900 \text{ m}^2/\text{g}$  contains  $6.7 \text{ wt\% H}_2\text{O}$  (calculated as  $2\text{SiOH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$ ) that would be lost upon dehydroxylation due to chemically bound OH alone. Such large OH contents are problematic when trying to prepare glasses by a sol-gel process that are identical to the corresponding melt-prepared composition (typical OH content  $\approx 500 \text{ ppm}$ ).

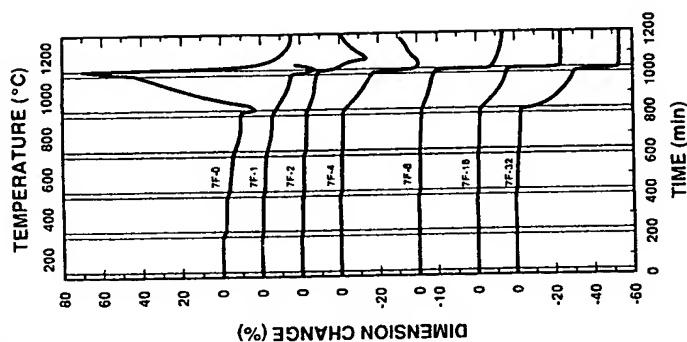
Although OH is removed through *condensation reactions*,



viscous sintering often commences before dehydroxylation is complete, leading to *bloating* or foaming of the gel in the final stages of sintering (see Fig. 8) [46]. Even if sufficient hydroxyl is removed so that sintering can occur without bloating, subsequent heating of the consolidated gel to its softening point, for example, during fiber drawing or sealing, may cause bloating. The hydroxyl content of consolidated gels is also detrimental to applications

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Fig. 8.



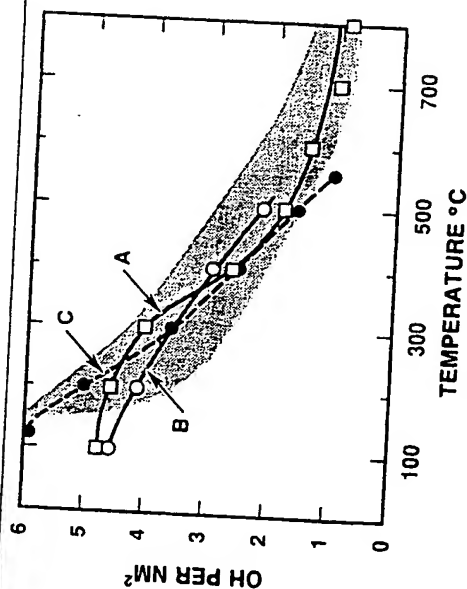
Dimensional change versus time for a series of silica gels containing 0-32 wt% F during an incremental heating procedure consisting of a sequence of isothermal hold temperatures between 200 and  $1200^\circ\text{C}$ . Bloating is denoted in the 7F-O sample (0 wt% F) by the dramatic expansion above  $800^\circ\text{C}$  [46].

related to optical communications where transparency in the IR port the spectrum is of utmost importance. This set of problems involving contents of gels has been the motivation to investigate means of dehydroxylation.

#### 3.1. Thermal Dehydroxylation

Thermal dehydroxylation relies on condensation reactions (Eq. 8) occurring on the gel surface. Thermal dehydroxylation of silicates has been investigated extensively, and summaries of numerous studies are reported by Iler [1]. Hydroxyl coverage versus temperature is shown in Fig. 9 for a var-

Fig. 9.



Hydroxyl coverage of the silica surface versus dehydroxylation temperature [1]. Shaded area: range of data on a variety of silicas investigated by Davydov *et al.* [36]. Dehydration [47]. Broken line, C: data on unannealed silica [48-51].

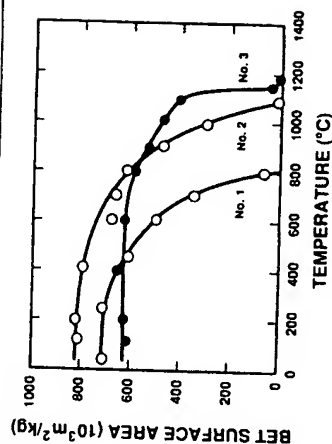
silicates heated in either air or vacuum. In general, OH groups are gradually lost with increasing temperature, but at 800°C where the extent of viscous sintering may be substantial (see, e.g., the surface area versus temperature data in Fig. 10), the OH coverage according to Fig. 9 is still about 1 OH/nm<sup>2</sup>. Thus thermal dehydroxylation is often not sufficient to avoid bloating in silica gels. For multicomponent systems that sinter at lower temperatures, the problem is even more severe, as discussed shortly.

The sequence of surface dehydration is the initial removal of physically adsorbed water at low temperatures followed by the progressive removal of weakly hydrogen bonded hydroxyls, strongly hydrogen bonded hydroxyls, and finally isolated hydroxyls. (See the schematic in Fig. 11.) It is postulated that the removal of isolated silanols occurs in part by diffusion of protons along strained siloxane bridges followed by condensation after an adjacent pair of hydroxyls is formed [1]. As previously discussed, two adjacent silanols that share a single bridging oxygen also appear "isolated" in vibrational spectroscopy. In this case condensation results in a highly strained, cyclic disiloxane species (Fig. 11).

Surface curvature may increase the extent of hydrogen bonding causing greater OH retention than anticipated from Fig. 9. For example, silica gels

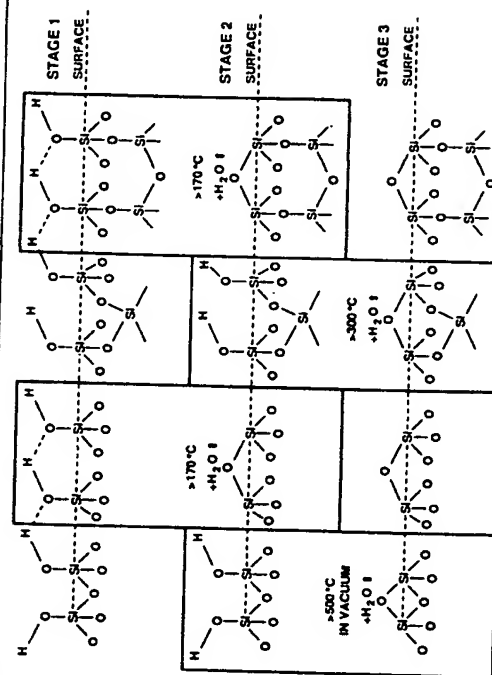
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Fig. 10.



BET surface area versus temperature for a series of silica gels with varying bulk densities ( $\rho_b$ , g/cm<sup>3</sup>) and pore diameters ( $d_p$ , Å) illustrating the effect of pore size on sintering temperature: No. 1,  $\rho_b = 1.34$  and  $d_p = 1.10$ ; No. 2,  $\rho_b = 1.10$  and  $d_p = 1.10$ ; No. 3,  $\rho_b = 0.60$  and  $d_p = 0.60$  [52].

Fig. 11.



Schematic illustration of various stages of surface dehydroxylation. Stage 1: removal of hydrogen bonded silanols resulting in four-membered and larger rings. Stage 2: condensation reactions between isolated silanols resulting in strained two- and three-membered rings. Stage 3: fully dehydroxylated surface.

with pore diameters of 1.0, 2.0, and 2.7 nm were dehydrated at a series of temperatures and their water contents measured [53]. The results compiled in Table 2 show that for small pore gels the OH coverages are considerably greater than indicated in Fig. 9, although values greater than  $4.9 \text{ OH/nm}^2$  presumably result from microporosity not accounted for in the BET surface area measurement.

The strategy for achieving extensive thermal dehydroxylation involves optimization of both the gel microstructure and the thermal processing conditions. Pertinent microstructural variables are pore size, surface area, and curvature. For any system the most beneficial microstructural improvement is increased pore size. Larger pores enhance the diffusion of the by-product,  $\text{H}_2\text{O}$ , and retard the sintering rate (proportional to surface area divided by pore size) allowing more complete dehydroxylation to occur prior to pore closure at the final stages of sintering. Pore size may be increased by any of several approaches: (1) the formation of large particles (pore size scales with particle size [54]); (2) particle aggregation [54]; (3) supercritical drying [55]; (4) stiffening of the network by increased condensation rates or aging [1], causing less shrinkage upon drying; and (5) double-dispersion procedures that produce hierarchical microstructures [56].

The effects of pore size on dehydroxylation are demonstrated by comparing the hydroxyl contents of silica aerogels and xerogels during heating and following complete consolidation by viscous sintering in a dry nitrogen ambient [55]. (See the Raman spectra in Fig. 12.) The S series of samples are xerogels prepared by a single-step acid-catalyzed hydrolysis of TEOS. The A series of samples are aerogels prepared by a two-step acid-base-catalyzed hydrolysis of TEOS followed by supercritical drying at  $300^\circ\text{C}$  and

Table 2.

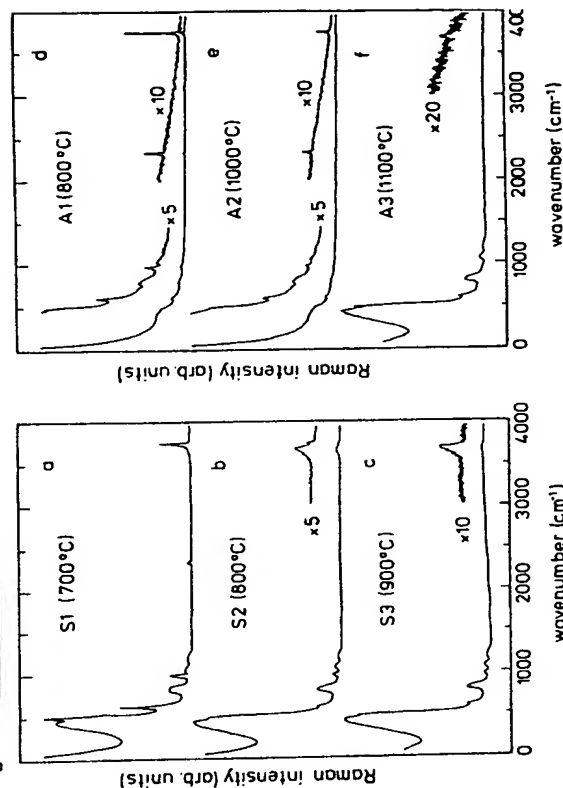
Hydroxyl Contents of Silica gels as a Function of Pore Diameter and Temperature.

Temperature of Dehydration ( $^\circ\text{C}$ )	Average Pore Diameter					
	10 Å		20 Å		27 Å	
	Area ( $\text{m}^2 \text{ g}^{-1}$ )	Bound $\text{H}_2\text{O}$ (%)	Area ( $\text{m}^2 \text{ g}^{-1}$ )	Bound $\text{H}_2\text{O}$ (%)	Area ( $\text{m}^2 \text{ g}^{-1}$ )	Bound $\text{H}_2\text{O}$ (%)
115	400	6.5	540	6.1	450	3.8
300	480	4.4	500	4.3	500	4.0
600	375	3.4	400	2.9	420	2.3
700	280	1.5	340	1.7	210	1.1

Source: Iler [1], Dzis'ko *et al.* [53].

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Fig. 12.



Raman spectra of silica xerogels (S series) and aerogels (A series) after dehydroxylation at temperatures between 700 and  $1100^\circ\text{C}$  [55].

$250 \text{ atm}$  spheres. Raman bands at  $3750$  and  $3680 \text{ cm}^{-1}$  are assigned to SiO-H stretching of isolated surface silanols and hydrogen bonded or bulk silanols, respectively. At  $800^\circ\text{C}$  the xerogel is nearly completely dense as evidenced by the greatly reduced relative intensity of the surface  $3750 \text{ cm}^{-1}$  band and the appearance of the bulk  $3680 \text{ cm}^{-1}$  band. The fully dense glass processed at  $900^\circ\text{C}$  contains a significant concentration of bulk silanols resulting from pore closure prior to complete dehydroxylation. By comparison the aerogel sample remains porous at  $1000^\circ\text{C}$  (there is no evidence of the bulk silanol band) allowing more complete dehydroxylation prior to densification at  $1100^\circ\text{C}$ . The hydroxyl content of the final densified glass is much less than that of the densified glass prepared from the xerogel.

Surface curvature is optimized by choosing synthesis conditions that result in particulate as opposed to polymeric microstructures. Particulate microstructures provide positive curvature surfaces (except in regions of neck

<sup>†</sup> Due to their varied environments and the close proximity of other species capable of hydrogen bonding, bulk silanols located within an amorphous network are characterized by broad bands at lower vibrational frequencies than isolated silanols.

formation) that are more easily dehydroxylated due to reduced hydrogen bonding, and minimize the surface to volume ratio, reducing the OH concentration on a per-gram basis. Smaller particles are beneficial from the standpoint of curvature, but they increase the surface area (and hence the OH content) and provide many more necks between particles, increasing the portion of the surface area exhibiting negative radii of curvature. Presumably an optimum (intermediate) particle size exists, but apparently no systematic investigation of this topic has been conducted. In any case, in order to facilitate dehydroxylation, it is wise to avoid synthesis conditions that produce microporous gels, characterized by small cylindrical pores.

Heat treatment procedures are designed to maximize the time spent at the highest possible temperatures prior to the onset of sintering and to minimize the water content of the processing ambient. The effects of heat treatment procedures on dehydroxylation are demonstrated by two related studies conducted by Gallo *et al.* [57] and Brinker and Haaland [58] on a borosilicate xerogel of nominal composition (wt%):  $83\text{SiO}_2$ ,  $15\text{B}_2\text{O}_3$ ,  $1.2\text{Na}_2\text{O}$ ,  $0.8\text{Al}_2\text{O}_3$ . Extensive dehydroxylation of such multicomponent systems is difficult in practice due to the low sintering temperature. (In this case, rapid sintering begins at about  $500^\circ\text{C}$ .)

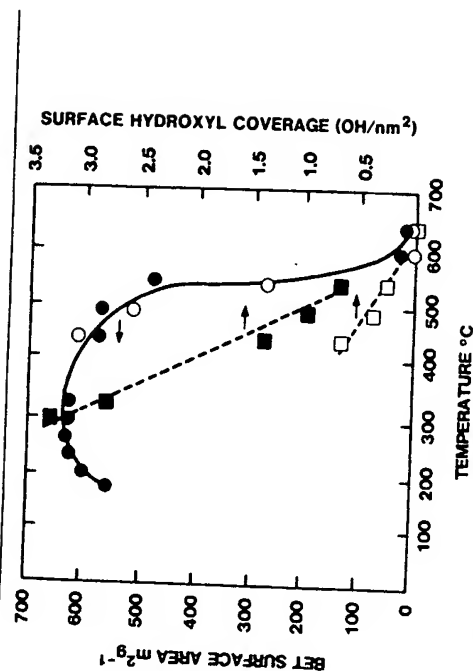
Figure 13 shows the BET surface area and hydroxyl coverage as a function of temperature for one series of samples heated at  $2^\circ\text{C}/\text{min}$  in ultrahigh-purity oxygen to temperatures between  $175$  and  $650^\circ\text{C}$  followed by quenching to room temperature (filled symbols) and a second series of samples heated to temperatures between  $400$  and  $650^\circ\text{C}$  followed by an 18-hour isothermal hold and quenching to room temperature (open symbols). OH/ $\text{nm}^2$  values were determined by combined IR and TGA techniques: (1) the OH content of the fully densified gel was measured by FTIR in transmission using an extinction coefficient of  $56\text{ l/mol-cm}$  [59];<sup>†</sup> (2) OH contents of the porous, quenched samples were then back-calculated for each sample from its weight loss, assuming that above  $300^\circ\text{C}$  all the weight loss was attributable to water. (The validity of this assumption was confirmed by Karl Fischer titration of the evolved gas.) The effect of the isothermal treatments at  $440$  and  $490^\circ\text{C}$  was to decrease the hydroxyl coverage while maintaining high surface areas. The surface area decreased at  $540^\circ\text{C}$ , but sufficient accessibility to the surface remained to allow a further reduction in the OH coverage. By  $595^\circ\text{C}$ , the accessible surface area for both series was reduced to about zero. Therefore  $540^\circ\text{C}$  appears to be the optimum processing temperature, although after an 18-hour hold a significant OH coverage remains.

<sup>†</sup>The low values of OH/ $\text{nm}^2$  obtained for this multicomponent borosilicate gel compared to pure silica gels may result from an inappropriate choice of extinction coefficient or may reflect a different surface structure.

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Fig. 13.

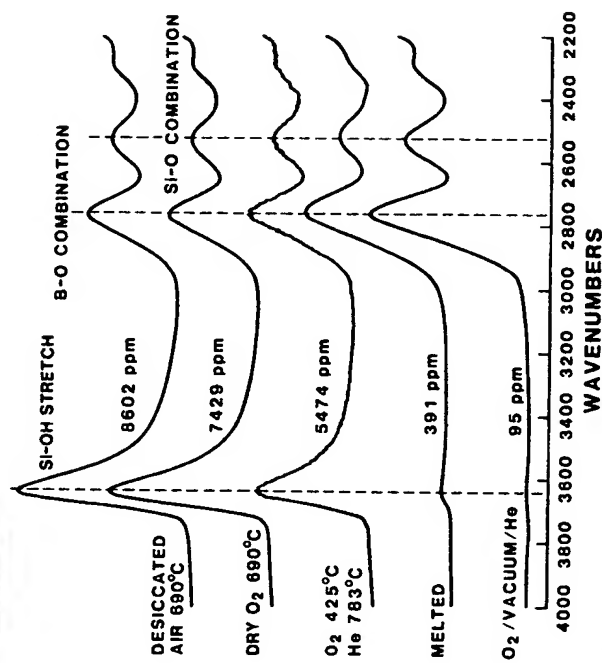


Variation of BET surface area (circles) and hydroxyl coverage (boxes) for multicomponent borosilicate samples during heating at  $2^\circ\text{C}/\text{min}$  (filled symbols; no isothermal hold); open symbols: 18-hour isothermal hold [57].

The effects of processing ambient on the residual hydroxyl content and shrinkage behavior are shown in Figs. 14 and 15 for the same multicomponent borosilicate composition investigated by Gallo *et al.* [57]. The hydroxyl contents determined by FTIR on fully dense samples (Fig. 14) exhibit a trend that reflects the water contents of the processing gases. Except for the vacuum treatment, the hydroxyl contents of the densified gels are considerably greater than for the corresponding melt-prepared glass. A corresponding trend is seen in the shrinkage behavior (Fig. 15): the onset of viscous sintering occurs at progressively higher temperatures for processing ambients that result in lower residual hydroxyl contents. As discussed in Chapter 11, this behavior is explained by an increase in gel viscosity that results from more extensive dehydroxylation when gels are processed in drier ambients.

The effect of dehydroxylation on the sintering temperature may be exploited to design an incremental heating procedure in which the gel is first held isothermally just below the sintering temperature. Dehydroxylation that occurs during the isothermal hold increases the sintering temperature so that a second higher isothermal heat treatment can be employed. Repeating this procedure several times allows more complete dehydroxylation to be achieved.

Fig. 14.



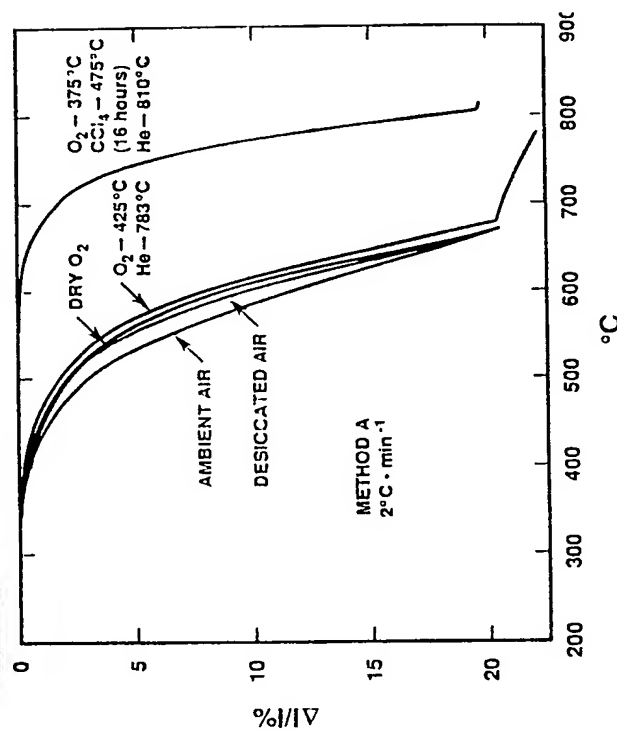
IR spectra of multicomponent borosilicate gels completely densified in various processing ambients compared to the IR spectrum of the corresponding melt-prepared composition. OH contents in ppm are determined using an extinction coefficient of 56 l/mol-cm. Further details concerning the heat treatments are given in Fig. 15 and in the text [58].

Such an incremental heat-treatment procedure was combined with a vacuum ambient ( $\sim 1 \times 10^{-7}$  torr using a cryopump) to effect quite low residual OH contents, as shown in Figure 14 (95 ppm, determined using an extinction coefficient of 56 l/mol-cm [59]). In addition to incremental heating, the effectiveness of the vacuum procedure relied on the quality of the vacuum (at such low pressure a monolayer of water is removed faster than it can form) and the capture characteristics of cryopumps which are very efficient in water removal compared to oil-diffusion pumps. A residual OH content of 95 ppm was sufficiently low to avoid bloating of the gel during forming procedures at temperatures near 1000°C. However, even with lower OH contents than melted glass, heat treatments in the vicinity of the softening point would occasionally cause the formation of a few small bubbles ( $\sim 1$  or  $2/\text{cm}^3$ ). This surprising appearance of bubbles may be due to the expansion of tiny, pre-existing, water-containing bubbles (invisible

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Fig. 15.



Linear shrinkage for a multicomponent borosilicate xerogel during heating at 2°C/min in various processing ambients. Dehydration and dealcalization ( $\text{CCl}_4$  treatment) increase sintering temperature [58].

to the naked eye) that were sealed off during the initial stages of dehydroxylation, although near IR spectroscopy showed no evidence of molecular water [58]. Perhaps bubble formation occurs at lower OH contents in sintered glass compared to melts because a few isolated pores present on a statistical basis<sup>1</sup> serve to efficiently nucleate bubble formation.

### 3.2. Chemical Dehydroxylation

The preceding section illustrates that thermal dehydroxylation normally does not reduce the OH content to ppb levels required, for example, for fiber optic preform manufacturing. For this reason, chemical dehydroxylation procedures, primarily employing halogens, have been widely investigated

<sup>1</sup> Unusually large pores that are not completely removed by sintering near  $T_g$ .